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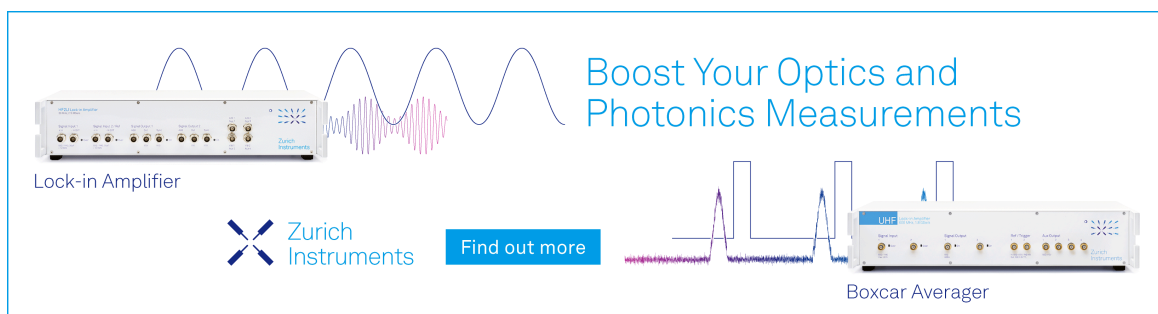View Online   Export Citation

First-principles definition of ionicity and covalency in molecules and solids

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ABSTRACT

The notions of ionicity and covalency of chemical bonds, effective atomic charges, and decomposition of the cohesive energy into ionic and covalent terms are fundamental yet elusive. For example, different approaches give different values of atomic charges. Pursuing the goal of formulating a universal approach based on firm physical grounds (first-principles or non-empirical), we develop a formalism based on Wannier functions with atomic orbital symmetry and capable of defining these notions and giving numerically robust results that are in excellent agreement with traditional chemical thinking. Unexpectedly, in diamond-like boron phosphide (BP), we find charges of +0.68 on phosphorus and −0.68 on boron atoms, and this anomaly is explained by the Zintl–Klemm nature of this compound. We present a simple model that includes energies of the highest occupied cationic and lowest unoccupied anionic atomic orbitals, coordination numbers, and strength of interatomic orbital overlap. This model captures the essential physics of bonding and accurately reproduces all our results, including anomalous BP.

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I. INTRODUCTION

All chemical systems are described by quantum mechanics, and all types of bonding have common origins in electronic exchange and correlation interactions, which fundamentally are of electrostatic nature. However, a full quantum-mechanical treatment of the electrons and nuclei is cumbersome and brings limited insight into such complex systems as molecules and solids. A more simplistic view, focusing on atoms and bonds, is particularly fruitful. Depending on how the electron density is redistributed, one obtains different types of bonding, such as ionic (with charged atoms and long-range interactions), covalent (with electron accumulation on bonds, and only short-ranged interactions), metallic (with nearly homogeneous valence electron density; this type of bonding can be viewed as an extreme case of multicenter covalent bonding), and van der Waals (weak interactions due to the inter-

actions between instantaneous atomic multipoles). These types of bonding can coexist—for example, van der Waals interactions exist in absolutely all chemical systems, and ionic bonding is always mixed with some degree of covalency. This simple classification has allowed researchers to understand an enormous range of facts and phenomena, including structures, spectra, and properties. Let us give some examples.

Covalent bonding is directional and results in low-coordination structures with high barriers of rearranging the structure and, consequently, widespread metastability. Three-dimensional networks of strong covalent bonds produce materials with the highest shear moduli and hardnesses. Metallic bonding is non-directional and produces structures with high coordination numbers, often based on close packings, with low barriers of phase transitions, low shear moduli, and low hardnesses. Ionic bonding is also non-directional, hence the tendency to form close-packed structures. Ionic crys-

tals obey Pauling's rules—for example, Pauling's third and fourth rules state that, to maximize electrostatic repulsion, the coordination polyhedra of highly charged cations avoid face- and edge-sharing (for covalent and metallic crystals, this is not the case).[1]

Due to the presence of long-range electrostatic interactions, peculiar phenomena are observed in ionic crystals—such as pyro-, piezo-, and ferroelectricity, where displacements of charged atoms (due to thermal expansion, strain, or phase transitions) create electric polarization. A vibration that involves charged atoms and leads to a change of the dipole moment strongly absorbs infrared (IR) radiation—and IR spectroscopy is one of the most convenient research tools. Strong infrared absorption by only molecules containing charged atoms explains why H_2O, CO_2, and CH_4 are greenhouse gases, while N_2 and O_2 (far more abundant in the atmosphere) are not. Related to these same long-range electrostatic interactions are the ionic contribution to dielectric constants of crystals and the LO–TO splitting in lattice dynamics.[2] To quantitatively describe these effects, Born dynamical charges[3] are introduced. These are rigorous but, in general, different from static charges that are needed to describe other properties.

Bond energy is another property directly related to the type of bonding and atomic charges. Indeed, it is well known that the formation of highly ionic compounds from low-ionicity substances is usually highly exothermic: e.g., in such reactions as $Na + 1/2Cl_2 = NaCl$, $Mg + 1/2O_2 = MgO$, or the reaction essential for energy needs of humanity: $CH_4 + 2O_2 = CO_2 + 2H_2O$.

Pauling[4] used this fact in 1932 for quantitatively defining electronegativity of the elements. To do that, he considered molecules with single bonds A–A, B–B, and A–B. Then, he assumed that the A–B bond energy is equal to the sum of covalent and ionic contributions,

$$E_{A-B} = (E_{A-B})_{cov} + (E_{A-B})_{ion}, \tag{1}$$

where the covalent energy of the bond A–B is assumed to be just the half-sum of the energies of homoatomic covalent bonds A–A and B–B,

$$(E_{A-B})_{cov} = (E_{A-A} + E_{B-B})/2, \tag{2}$$

and the ionic energy (in units of electron-volts) is assumed to be equal to the squared difference of electronegativities χ of atoms A and B,

$$(E_{A-B})_{ion} = (\Delta\chi_{A-B})^2. \tag{3}$$

Having thus defined electronegativities, Pauling[2] then proposed a way to calculate the degree f_i of ionicity of a bond (which is the ratio of actual atomic charges to formal ionic charges),

$$f_i = 1 - \exp\left[(-\Delta\chi)^2/4\right]. \tag{4}$$

This formula correctly implies that fully ionic bonds do not exist, but the degree of ionicity approaches 1 (i.e., 100%) as $\Delta\chi$ increases.

The mixing of ionic and covalent components in the total bond energy leads to the following result:[5]

$$E_{A-B} = f^2_i (E_{A-B})_{ion} + (1 - f^2_i)^{1/2}(E_{A-B})_{cov}. \tag{5}$$

Pauling's approach is extremely simple and to first order explains many phenomena. The concept of electronegativity turned out to be very fruitful.[1,4,6–14] However, Pauling's original approach has deficiencies. For some atoms, it is problematic to find a reliable energy of the homoatomic single bond. The underlying assumptions of Pauling's approach are arbitrary. Even worse, for predominantly ionic bonds, Eq. (3) overestimates the ionic part of bond energies by several times.[15]

Recently, Tantardini and Oganov[6] proposed an improved thermochemical scale of electronegativities. They noted that Eq. (4) contains an unphysicality—it defines the degree of ionicity solely by the ionic contribution to the bond energy, whereas in reality, the ratio of ionic to covalent contributions is relevant. For example, one expects 50% ionicity when ionic and covalent contributions are equal. This suggests that it is better to set, at variance with Eq. (3),

$$(\Delta\chi_{A-B})^2 = (E_{A-B})_{ion}/(E_{A-B})_{cov}. \tag{6}$$

This immediately leads to the formula for bond energy,

$$E_{A-B} = (E_{A-B})_{cov}[1 + (\Delta\chi_{A-B})^2], \tag{7}$$

which has been used[4] for creating a new scale of electronegativities. The degree of ionicity can be described with these new electronegativities by the following formula:

$$f_i = 1 - \exp\left[-(\Delta\chi)^2/k\right], \tag{8}$$

where k = 1.4427 is obtained without any fitting, just by requiring that when ionic and covalent contributions are equal (i.e., when $(\Delta\chi)^2 = E_{ion}/E_{cov} = 1$), the degree of ionicity should be 50%. The approach of Tantardini and Oganov is more robust but still relies on a rather arbitrary definition of the covalent contribution (2) and formula (7) is purely heuristic.

One could conclude that, with the multitude of different definitions, atomic charge is a very vague concept—but such a view would be incorrect. Meister and Schwarz[16] showed that all the numerous definitions of the atomic charge (based on the population analysis of the wavefunction, electron density partitioning, electrostatic potentials, dipole moments, IR intensities, chemical shift of core electron ionization energies, x-ray emission and absorption spectra, LO–TO splitting and Born charges, bandgaps, dielectric constants, piezoelectric constants, energy surfaces, Szigeti method,[17] etc.) are strongly interrelated. Performing principal components analysis of the charges determined with 29 different ways, these authors showed that this dataset has only one significant principal component. This means that there is one single concept underlying all these definitions of the atomic charge. Moreover, being directly related to so many diverse properties, this concept is extremely useful and fundamental.

This elusive concept must be derivable quantum-mechanically. Here, we develop a theory enabling the first-principles quantum-mechanical calculation of ionic and covalent terms in the cohesive energy, as well as of atomic charges. This theory is based on the Wannier function formalism.[18,19]

II. METHOD

Wannier functions promise to be a new foundation of the theory of chemical bonding. For example, Jiang *et al.*[20] have provided a

rigorous definition of the oxidation number based on Wannier functions. Interestingly, their definition was dynamic (involving moving the atoms), whereas a simpler static quantum-mechanical definition probably can be formulated, but this has not been achieved yet. Such a static definition is likely to exist because oxidation numbers determine, for example, the stoichiometries of compounds.

Here, we formulate a static quantum-mechanical approach, allowing one to extract atomic charges and calculate the ionic and covalent contributions of the bond energy.

Let us consider a binary compound AB. Its chemical bonding energy E_{bond} is usually defined as a difference of total energies of the compound per formula unit at equilibrium volume V_0 and a sum of the energies of free atoms A and B at infinity,

$$E_{bond}^0 = E_{AB}^0 - (E_A^\infty + E_B^\infty). \tag{9}$$

From density functional theory solution, one obtains a set of electronic eigenvalues and eigenfunctions $\epsilon_{\vec{k}}^\alpha, |\psi_{\vec{k}}^\alpha\rangle$ and the electron Hamiltonian can be written as

$$\hat{H} = \sum_{\vec{k}\alpha} |\psi_{\vec{k}}^\alpha\rangle \epsilon_{\vec{k}}^\alpha \langle\psi_{\vec{k}}^\alpha| \tag{10}$$

with the corresponding density matrix operator

$$\hat{\rho} = \sum_{\vec{k}\alpha} |\psi_{\vec{k}}^\alpha\rangle n_{\vec{k}}^\alpha \langle\psi_{\vec{k}}^\alpha|, \\ n_{\vec{k}}^\alpha = \theta(E_{Fermi} - \epsilon_{\vec{k}}^\alpha). \tag{11}$$

Wannier functions $|W_i\rangle$ are calculated by the unitary transformation of Bloch function set $|\psi_{\vec{k}}^\alpha\rangle$,

$$|W_i\rangle = \sum_{\vec{k}\alpha} |\psi_{\vec{k}}^\alpha\rangle\langle\psi_{\vec{k}}^\alpha|\phi_i\rangle, \tag{12}$$

where $|\phi_i\rangle$ are trial atomic wave functions and, hence, $|W_i\rangle$ also have the same atomic orbital symmetry. A basis set $|W_i\rangle$ defined by Eq. (12) is then orthonormalized. One can say that Wannier functions $|W_i\rangle$ are "natural" atomic orbitals for electrons in a crystal and index i runs over atomic quantum numbers nl ($1s, 2s, 2p, 3p, 3d, \ldots$). Equation (12) is one of the possible choices for unitary transformation of Bloch function set $|k\rangle$, and it was chosen to obtain Wannier functions having the symmetry of atomic orbitals as is usually done in the analysis of chemical bond. It is known that Wannier functions are not unambiguously defined. The projection procedure in Eq. (12) solves this problem, giving uniquely defined Wannier functions that are most similar to atomic orbitals, fully compatible with both atomic limit and solid-state calculations, and enabling us to separate atomic and bonding effects.

Wannier functions $|W_i\rangle$ Eq. (12) are in real space representation. Sometimes, it is useful to define the reciprocal space representation $|W_i^{\vec{k}}\rangle$ for them,

$$|W_i^{\vec{T}}\rangle = \sum_{\vec{k}} \exp(-i\vec{k}\vec{T})|W_i^{\vec{k}}\rangle, \\ |W_i^{\vec{k}}\rangle = \sum_\alpha |\psi_{\vec{k}}^\alpha\rangle\langle\psi_{\vec{k}}^\alpha|\phi_i\rangle. \tag{13}$$

Here, $\vec{T}$ is the translation vector, i is an atomic number in the crystal unit cell, and α is a band number.

One can redefine the Hamiltonian and density matrix in a Wannier function basis,

$$\hat{H} = \sum_{\vec{k}} \sum_{ij} |W_i^{\vec{k}}\rangle H_{ij}^{\vec{k}}\langle W_j^{\vec{k}}|, \\ \hat{\rho} = \sum_{\vec{k}} \sum_{ij} |W_i^{\vec{k}}\rangle Q_{ij}^{\vec{k}}\langle W_j^{\vec{k}}|. \tag{14}$$

Then, the electronic energy E is

$$E = \text{Tr}(\hat{\rho}\hat{H}) = \sum_{\vec{k}} \sum_{ij} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}} \\ = \sum_{\vec{k}} \sum_i Q_{ii}^{\vec{k}} H_{ii}^{\vec{k}} + \sum_{\vec{k}} \sum_{ij,i\neq j} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}}. \tag{15}$$

To separate the electronic energy E in Eq. (15) into covalent and ionic parts is not a trivial task. While the interatomic term $\sum_{\vec{k}}\sum_{ij,i\neq j} Q_{ij}^{\vec{k}} H_{ji}^{\vec{k}} = \sum_{ij,i\neq j} E_{ij}$ is clearly a covalent energy, the diagonal in the atomic index term $\sum_i E_{ii} = \sum_{\vec{k}}\sum_i Q_{ii}^{\vec{k}} H_{ii}^{\vec{k}}$ contains both contributions: covalent energy for all atoms of type i in crystal and ionic part of energy. To separate them, let us introduce the average energy $H_i = \sum_{\vec{k}} H_{ii}^{\vec{k}}$ and average occupancy $Q_i = \sum_{\vec{k}} Q_{ii}^{\vec{k}}$ for atom i. The ionic part can be defined as $E_i^{ion} = Q_i H_i$, and the covalent part can be defined as $E_i^{cov} = E_{ii} - Q_i H_i$. The electronic energy E in Eq. (15) can be written as

$$E = E^{cov} + E^{ion}, \\ E^{ion} = \sum_i E_i^{ion} = \sum_i Q_i H_i, \\ E^{cov} = \sum_{ij,i\neq j} E_{ij} + \sum_i E_{ii} - \sum_i Q_i H_i. \tag{16}$$

In a general case with orbital indexes $L = (l, m)$, Eq. (15) is

$$E = \text{Tr}(\hat{\rho}\hat{H}) = \sum_{\vec{k}} \sum_{iL,jL'} Q_{iL,jL'}^{\vec{k}} H_{jL',iL}^{\vec{k}} \\ = \sum_{\vec{k}} \sum_{iL,iL'} Q_{iL,iL'}^{\vec{k}} H_{iL',iL}^{\vec{k}} + \sum_{\vec{k}} \sum_{iL,jL'} Q_{iL,jL'}^{\vec{k}} H_{jL',iL}^{\vec{k}}. \tag{17}$$

For binary compound AB, the chemical bonding energy [Eq. (9)] is

$$E_{bond} = E_{AB} - (E_A^\infty + E_B^\infty) \\ = E^{cov} + E^{ion} - (H_A^\infty Q_A^\infty + H_B^\infty Q_B^\infty). \tag{18}$$

The following approximation could be useful:

$$H_A^\infty = H_A = \sum_{\vec{k}} H_{AA}^{\vec{k}}, \\ H_B^\infty = H_B = \sum_{\vec{k}} H_{BB}^{\vec{k}}. \tag{19}$$

Then, from Eqs. (18) and (16),

$$E_{bond} = E^{cov} + E^{ion} - (H_A Q_A^\infty + H_B Q_B^\infty),$$
$$E^{ion} = E_A^{ion} + E_B^{ion} = Q_A H_A + Q_B H_B, \quad (20)$$
$$E^{cov} = 2E_{AB} + E_{AA} - Q_A H_A + E_{BB} - Q_B H_B.$$

Hence, the bonding energy separation is

$$E_{bond} = E_{bond}^{cov} + E_{bond}^{ion},$$
$$E_{bond}^{ion} = E_A^{ion} + E_B^{ion} - (H_A Q_A^\infty + H_B Q_B^\infty)$$
$$= (Q_A - Q_A^\infty) H_A + (Q_B - Q_B^\infty) H_B, \quad (21)$$
$$E_{bond}^{cov} = E^{cov} = 2E_{AB} + E_{AA} - Q_A H_A + E_{BB} - Q_B H_B.$$

The covalent contribution to the bonding energy E_{bond}^{cov} in Eqs. (20) and (21) contains, by definition [see Eq. (16)], only off-diagonal terms of Hamiltonian and density matrices in the Wannier basis having atomic orbital symmetry [Eq. (14)]. Hence, it directly corresponds to the usual chemical understanding of covalent bond between atomic orbitals. However, the ionic part is defined by contribution from diagonal terms of those matrices minus $(H_A Q_A^\infty + H_B Q_B^\infty)$ term. Hence, it contains not only an ion–ion interaction in crystal but also the energy of transferring the electrons to/from the neutral atoms forming charged ions.

III. COMPUTATIONAL DETAILS

All DFT calculations were conducted using the Quantum ESPRESSO suite with the standard solid-state pseudopotentials (SSSP) Perdew–Burke–Ernzerhof (PBE) Precision v1.3.0 library.[21,22] The kinetic energy cutoff for the plane wave wavefunction expansion was set according to the recommendations provided in the SSSP library for each element. An integration in the reciprocal space was performed on a regular $16 \times 16 \times 16$ k-point mesh covering the Brillouin zone. The construction of Wannier function basis and the determination of the Hamiltonian and occupation matrix elements were carried out using the wannier_ham.x[19] code integrated into Quantum ESPRESSO. Only Wannier functions with the symmetry of s- and p-atomic orbitals of the outermost electronic shell for each ion were considered. To separate the electronic energy into covalent and ionic parts, we employed an in-house Python script implementing Eqs. (20) and (21).

IV. RESULTS AND DISCUSSION

Table I gives the atomic charges (calculated as occupancy numbers of the corresponding Wannier functions) and the ionic and covalent parts of the cohesive energy for a number of relatively simple substances. One can see the following:

(1) The degree of ionicity (which is usually defined as the ratio of effective charges of the atoms to their valence) and the ratio of the ionic to covalent energy components increase as the electronegativity difference increases. For example, elemental silicon has 0% ionicity, AlN is 35% ionic, whereas the degree of ionicity is equal to 57% for LiH, 81% for NaCl, and 83% for CsF. All of this is fully consistent with chemical intuition. Some results are less intuitive: zinc blende (ZnS) has just 1.5% degree of ionicity.

(2) Zinc blende-type BP is very much anomalous, having inverse charges, opposite to what is expected from atomic electronegativities: The B atom has a negative charge of −0.68, whereas the P atom has a positive charge of +0.68. Unexpectedly, the degree of covalency exceeds 100% (it equals 102%) and the ionic contribution to the cohesive energy is positive (destabilizing). These anomalies require an explanation. We note that the ionic contribution is defined here as a sum of the electrostatic (Madelung) energy and the energy of modifying the atoms from neutral (as in isolated atoms) to charged (as in the crystal). Wherever the ionic contribution is positive, the degree of covalency is greater than 100%. The ionic contribution is positive only when the energy of modifying atomic wavefunctions is so positive that it outweighs the Madelung energy. For BP with inverted charges (positive for P and negative for B), moving electrons from lower-energy orbitals of P to higher-energy orbitals of B increases the energy and results in a positive ionic term—however, this unfavorable charge transfer serves to strengthen covalent bonding.

(3) We also observe inverted ionic charges for the CO molecule. The atomic charges in CO molecule have been addressed in numerous studies, and it was established that its dipole moment corresponds to inverted charges, negative for C and positive for O.[23] This has interesting consequences—e.g., F–H. . . .C–O hydrogen bond complexes, where, indeed, the C atom of the CO molecule plays the role of a negatively charged atom.[24] Similarly, CO molecules adsorb on metallic clusters so that the carbon atom is in direct contact with metal atoms.[25] Such inverted charges can be easily understood using the Zintl–Klemm rule: atom of group N, when losing an electron structurally, behaves like an atom of group N−1 and, when gaining an electron, behaves like an atom of group N+1. The carbon atom can form *four* bonds, but oxygen can only form *two* bonds; thus, the simplest electronic structure C=O leaves two valences of carbon unused. If the oxygen atom loses an electron to carbon (which by itself is unfavorable), we get O^+ and C^- atoms, each of which is isoelectronic to the nitrogen atom and capable of forming *three* covalent bonds in the molecule $C^- \equiv O^+$—and this is much more favorable, as it enables much stronger covalent bonding.

(4) Effective atomic charges (Table I) are significantly smaller than the formal ionic charges corresponding to the atomic valence. Ionic energy must be proportional to the square of the ionic charges Z, as in the Madelung formalism, so the percentage of ionic contribution to the bond energy should be defined by the value of $(Z/Z_0)^2$, where Z_0 is the formal ionic charge. In Table II, we compare this simple estimation with the full calculation using formula (21). The agreement is remarkably good. This means that the reduction of ionic charges from the formal values due to covalency could serve as a good estimation of the percentage of ionic and covalent contributions to the bond energy.

A. The peculiar case of BP

The result for BP with the reversed cation–anion charges (+0.68 on phosphorus and −0.68 on boron ions) looks unusual and

TABLE I. Atomic charges and contributions to bond energies for select crystalline compounds and CO molecule.

Compound	Structure type and space group	Atomic charges	E_{ion} (eV/f.u.)	E_{cov} (eV/f.u.)	E_{bond} (eV/f.u.)	$R = E_{cov}/E_{bond}$
LiF	Rock salt (Fm-3m)	Li: 0.70, F: −0.70	−7.410	−7.508	−14.918	0.50
NaF	Rock salt (Fm-3m)	Na: 0.87, F: −0.87	−8.708	−2.824	−11.531	0.24
KF	Rock salt (Fm-3m)	K: 0.87, F: −0.87	−7.161	−2.189	−9.349	0.23
RbF	Rock salt (Fm-3m)	Rb: 0.90, F: −0.90	−6.963	−1.534	−8.496	0.18
CsF	Rock salt (Fm-3m)	Cs: 0.83, F: −0.83	−5.375	−2.335	−7.710	0.30
LiH	Rock salt (Fm-3m)	Li: 0.57, H: −0.57	−2.625	−6.637	−9.261	0.72
Si	Diamond (Fd-3m)	Si: 0	−0.000	−37.371	−37.371	1.00
BP	Zinc blende (F-43m)	B: −0.68, P: 0.68	0.815	−50.648	−49.833	1.02
NaCl	Rock salt (Fm-3m)	Na: 0.81, Cl: −0.81	−5.918	−3.176	−9.094	0.35
KBr	Rock salt (Fm-3m)	K: 0.76, Br: −0.76	−4.333	−3.159	−7.492	0.42
KI	Rock salt (Fm-3m)	K: 0.76, I: −0.76	−3.842	−2.791	−6.633	0.42
AlN	Zinc blende (F-43m)	Al: 1.06, N: −1.06	−7.833	−45.393	−53.226	0.85
BN	Hexagonal (P6_3/mmc)	B: 0.52, N: −0.52	−2.760	−64.179	−66.939	0.96
CaF$_2$	Fluorite (Fm-3m)	Ca: 1.33, F: −0.67	−13.155	−14.585	−27.740	0.53
ZnS	Zinc blende (F-43m)	Zn: 0.03, S: −0.03	−0.118	−34.490	−34.608	1.00
MgO	Rock salt (Fm-3m)	Mg: 1.66, O: −1.66	−13.606	−6.880	−20.487	0.34
MgS	Rock salt (Fm-3m)	Mg: 1.60, S: −1.60	−7.984	−5.335	−13.320	0.40
Al$_2$O$_3$	Corundum (R-3c)	Al: 1.84 O: −1.23	−33.024	−61.696	−94.720	0.65
SiO$_2$	α-quartz (P3_12-1)	Si: 2.65, O: −1.33	−23.678	−34.339	−58.017	0.59
CO molecule		C: −0.52, O: 0.52	−3.683	−23.022	−26.705	0.86

TABLE II. Atomic charges and estimates of the degree of ionicity. Degree of ionicity is usually defined as the ratio of the effective atomic charge to the formal charge. Coulomb energy is then proportional to the square of the degree of ionicity, and we, indeed, see a close similarity between the ionic contribution to binding energy and the square of the degree of ionicity.

Compound	Atomic charges	Z/Z_0	$(Z/Z_0)^2$	$1 − E_{cov}/E_{bond}$
LiF	Li: 0.70, F: −0.70	0.7	0.49	0.50
NaF	Na: 0.87, F: −0.87	0.87	0.76	0.76
KF	K: 0.87, F: −0.87	0.87	0.76	0.77
RbF	Rb: 0.90, F: −0.90	0.9	0.81	0.82
CsF	Cs: 0.83, F: −0.83	0.83	0.69	0.70
LiH	Li: 0.57, H: −0.57	0.57	0.32	0.28
NaCl	Na: 0.81, Cl: −0.81	0.81	0.65	0.65
KBr	K: 0.76, Br: −0.76	0.76	0.58	0.58
KI	K: 0.76, I: −0.76	0.76	0.58	0.58
AlN	Al: 1.06, N: −1.06	0.35	0.13	0.15
BN	B: 0.52, N: −0.52	0.17	0.03	0.04
CaF$_2$	Ca: 1.33, F: −0.67	0.67	0.45	0.47
ZnS	Zn: 0.03, S: −0.03	0.03	0	0
MgO	Mg: 1.66, O: −1.66	0.83	0.69	0.66
MgS	Mg: 1.60, S: −1.60	0.8	0.64	0.60
Al$_2$O$_3$	Al: 1.84 O: −1.23	0.61	0.37	0.35
SiO$_2$	Si: 2.65, O: −1.33	0.67	0.44	0.41

requires explanation. In all electronegativity scales, phosphorus is more electronegative than boron and should attract electrons from boron onto itself, but we see exactly the opposite. Let us explain this anomaly. Consider the case of neutral B and P atoms; in the covalent case, each of these atoms can form three ordinary (2-center 2-electron) bonds. If we form (at first counterintuitive) B$^-$ and P$^+$ ions, then each of these ions can form four bonding electron pairs (four ordinary covalent bonds), thus strengthening covalent bonding. If the increase in energy due to the formation of these inverse charges (which is what makes E_{ion} of BP positive; see Table I) is outweighed by the effect of covalent bond strengthening, then inverse charges will be formed. BP can also be understood on the basis of the Zintl–Klemm rule, which draws a structural analogy between charged atoms and neutral atoms of other groups in the Periodic Table.

Here, we talk about the occupation numbers for the Wannier functions contrary to an integrated charge inside some atomic spheres. The squared Wannier functions (representing corresponding charge distribution) for boron and phosphorous along the B–P bond are shown in Fig. 1. It is clear that the Wannier function for P (Fig. 1, central panel) is much more compact, and its charge is very small at the B–P bond midpoint. The squared Wannier function for the boron atom (Fig. 1, left panel) is more spread out and has a nonzero contribution in the region close to the P ion. This means that the electrons located near the phosphorus atom in BP originate partially from the spatially extended states of the boron atom.

At the same time, if one takes a look at the charge density corresponding to the bonding molecular orbital (Fig. 1, right panel), which corresponds to a linear combination of the anion and the cation Wannier functions, there is no contradiction with the traditional picture of asymmetric covalent bonding: the charge density maximum is, indeed, located closer to the phosphorus ion.

That is, phosphorus is more electronegative than boron, as it should be. An analysis of the orbital occupation numbers gives the
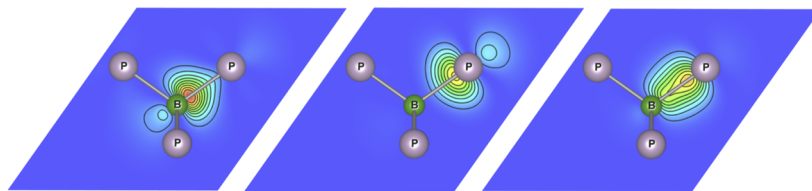
FIG. 1. Section of the squared Wannier functions centered on the boron (left panel) and phosphorous (central panel) ions. Right panel: Section of the squared bonding molecular orbital.

same conclusions. For a boron ion, the occupation of the sp^3 orbital is 0.92, and for phosphorus it is 1.08. Therefore, the orbitals of boron are less populated than the orbitals of phosphorus. For the whole atom, the number of valence electrons for boron is 3.68, and for phosphorus, it is 4.32. Consequently, the phosphorus ion has 0.64 more electrons than the boron ion, as should be for a more electronegative ion. However, compared to neutral atoms (which have 3 and 5 valence electrons for B and P, respectively), we obtain +0.68 charge on P and −0.68 on B atoms.

We consider static charges, related to redistribution of charge density as a result of chemical bonding. Earlier, it was calculated that Born dynamical charges (related to polarization induced by atomic displacements) show the same anomaly in BP and related compounds: these charges on the B atom are −0.75 in BP, −0.57 in BAs, and −1.30 in BSb.[26]

The explanation of the paradox is very simple: if one imagines the limit of purely covalent bonding with equal sharing of the electrons between B and P atoms in this tetrahedral structure, this will imply four valence electrons on each atom and automatically lead to the charge of −1 on B and +1 on P atoms. Note that since in the purely covalent case the charges are non-zero, the usually assumed relationship between the charges and the degree of ionicity (f = Q/Z) is a gross simplification. Note also that the electronegativity difference will lead to redistribution of electron density (shifting it to the more electronegative phosphorus atom) and change the atomic charges. Both of these effects need to be considered to get quantitative results. To delve deeper into the physics of our results, we developed a simple model.

B. Simple two-orbital model

All the results presented in Table I for compounds with various types of bonding can be described with a simple and straightforward model including only two orbitals.

The most important parameters in our calculation scheme are H_A, H_B—atomic energies [diagonal terms of the Hamiltonian equation (14)] or their difference $\Delta E = H_A - H_B$ and off-diagonal Hamiltonian matrix terms $H_{AB} = t$. The first one determines the tendency to form ions from neutral atoms, and the second one is responsible for the covalent bonding between the atoms. It is useful to consider the simplest model containing these parameters and compare it with our full calculation results. We will use notation orbital 1 for atom A and orbital 2 for atom B.
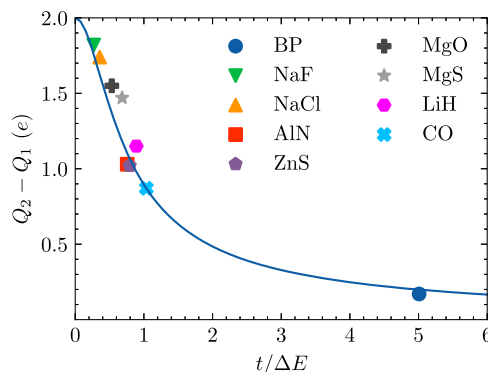

FIG. 2. Difference of orbital occupations for the model (solid line). Mapping of the results of DFT calculation onto the two-band model (symbols).

Let us assume that we have two different atoms with one partially filled orbital on each atom (two electrons in total). Then, the Hamiltonian of the system is

$$H = \begin{pmatrix} E & t \\ t & E - \Delta E \end{pmatrix}, \qquad (22)$$

where E is the energy level of the first orbital (the higher one) and the second atom has the orbital energy which is ΔE lower than the first one. The hopping energy t describes hybridization between the orbitals. From the eigenvectors of the model Hamiltonian matrix [Eq. (22)], one can get occupation numbers for two orbitals (Q_1 and Q_2) and then calculate the charge transfer $Q_2 - Q_1$ from the first to the second atom. The corresponding curve as a function of the ratio $t/\Delta E$ is presented in Fig. 2. One can see that the larger the $t/\Delta E$ value, the smaller is charge transfer $Q_2 - Q_1$ that characterizes ionicity.

At first, we apply this model to LiH, which is very close to the model: both atoms have a non-degenerate s-orbital with one electron on them for neutral atoms. The essential difference is that every atom has not one but six bonds with the other type atoms in its rock salt crystal structure, or in other words, the number of hybridization channels $N = 6$. From perturbation theory, it is known that having several equivalent hybridization channels can be

approximated in single orbital per atom model by using the effective hybridization term calculated as $\sqrt{N}t$. We take the E, ΔE, and t parameters from diagonal and off-diagonal elements of the calculated Hamiltonian matrix for LiH in the Wannier function basis. The charge transfer $Q_H - Q_{Li}$ obtained in our Wannier function formalism lies very close to the model curve. The same mapping of the model was done for other compounds with the rock salt crystal structure: NaF, NaCl, MgO, and MgS (see Fig. 2) with good results showing these compounds to be predominantly ionic having the ratio $t/\Delta E < 1$.

The last three compounds AlN, BP, and ZnS have the zinc blende type structure usual for semiconductors. For them, $Q_2 - Q_1$ was calculated for a single sp^3 orbital pair. In the pair, an orbital of the first atom is oriented directly to the orbital of the neighboring atom and the corresponding interaction has the largest hopping t value. The comparison with the model curve is also very good, giving mixed ionic–covalent nature of bonding.

The atomic charges can be calculated from $Q_2 - Q_1$ in the following way: $I_1 = Q_1^\infty - Q_1$, $I_2 = -I_1$, $I_1 = ((Q_2^\infty - Q_1^\infty) - (Q_2 - Q_1))/2$, where Q_1^∞ and Q_2^∞ are occupations for the corresponding neutral atoms. (Please note that for the zinc blend type structure, total atomic occupancy can be obtained from single orbital occupancy by multiplying it on 4 that is a number of sp^3 orbitals).

For BP, this formula gives a negative charge of -0.68 for boron and a positive charge of $+0.68$ for phosphorus because covalency is strong enough (and the ratio $t/\Delta E$ is much larger than 1) to make the total number of electrons on boron is 3.68 (larger that its neutral atom value $Q_B^\infty = 3$), while for phosphorus, it is equal to 4.32 (smaller than $Q_P^\infty = 5$).

V. CONCLUSIONS

We present a first-principles procedure for determining effective atomic charges and perform decomposition of the cohesive energy into ionic and covalent terms based on the Wannier function formalism. This method was applied to various compounds with typical ionic, covalent, and mixed bonding nature and has shown good results. In diamond-like BP, we find "inverse" charges of $+0.68$ on phosphorus and -0.68 on boron atoms, which agrees well with earlier calculated Born dynamical charges[26] (related to polarization induced by atomic displacements). We explain why the same anomaly is present also in static charges, and our explanation is based on the Zintl–Klemm rule and the tendency to maximize the covalent bonding strength. We develop a simple model, including the energy difference between the orbitals of the interacting atoms and the strength of their hybridization. The effective charges obtained in our Wannier calculations agree very well with this model.

It will be interesting to apply our approach to various non-trivial cases, such as:

(1) Donor–acceptor bonds (where the more electronegative atom donates an electron pair to form a bond with a less electronegative atom, somewhat similar to what we discussed for BP). Hydrogen bonds are an important case of such bonds.
(2) Compounds with high oxidation states (such as $KMnO_4$[27]).

(3) Exotic high-pressure compounds, such as Na_3Cl, Na_2Cl, $NaCl_7$,[28] and Na_2He.[29]

AUTHOR DECLARATIONS
Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Vladimir I. Anisimov: Conceptualization (equal); Methodology (equal); Supervision (equal); Writing – review & editing (equal). **Artem R. Oganov**: Funding acquisition (lead); Investigation (equal); Project administration (lead); Writing – review & editing (equal). **Dmitry M. Korotin**: Formal analysis (equal); Investigation (equal); Software (lead); Writing – review & editing (equal). **Dmitry Y. Novoselov**: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **Alexey O. Shorikov**: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **Alexander S. Belozerov**: Formal analysis (equal); Investigation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

All data supporting the findings of this work are included in the main text. Additional data will be made available on request.

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